Shell Global Solutions

Method for Determining the Environmental Significance of Vapor-Only Releases

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SAM Forum and Symposium

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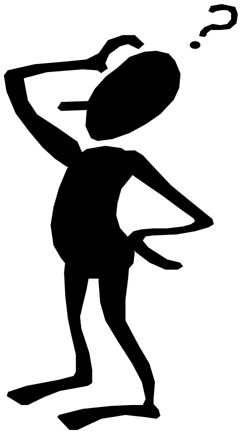
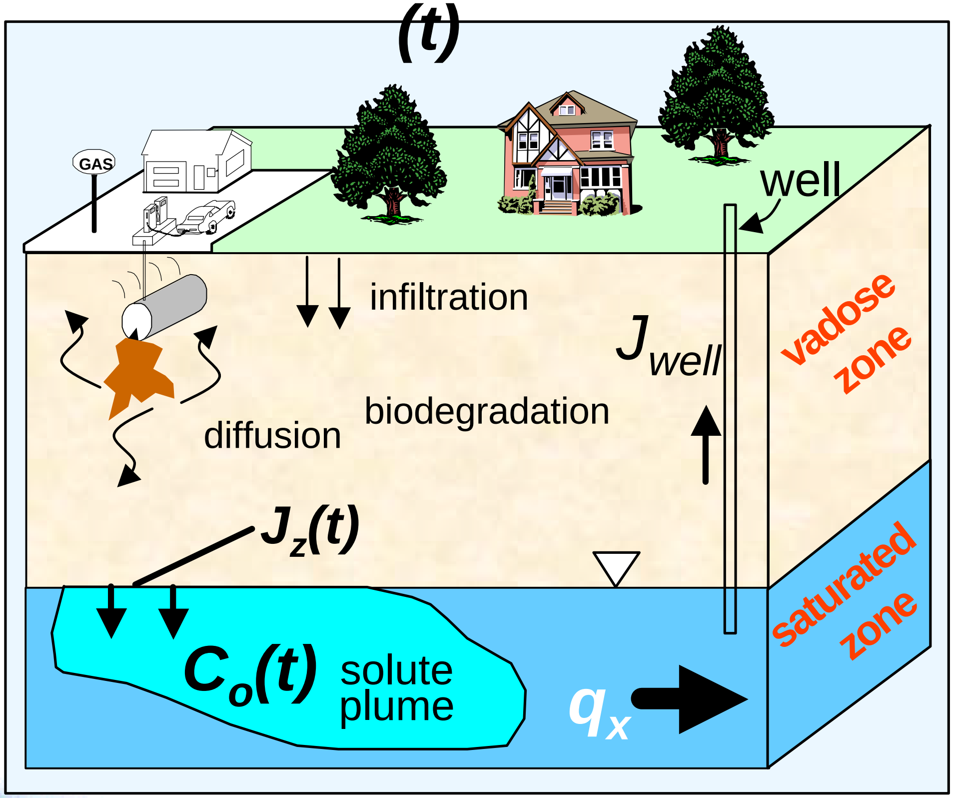
Some Considerations

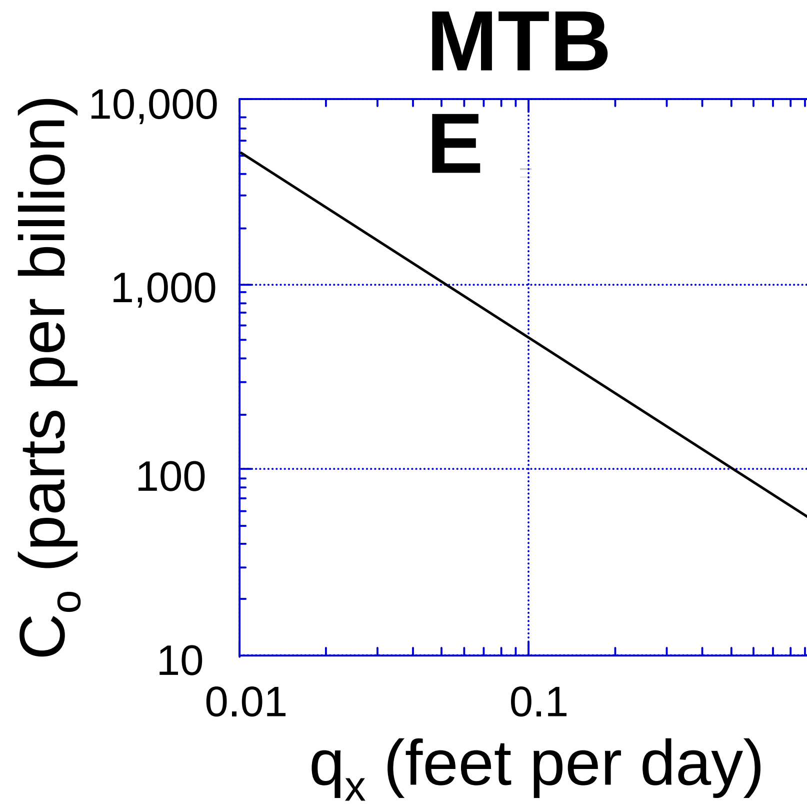
- Vapor (or small-volume liquid) release identified -- what does it mean?
- Environmental significance different for different gasoline compounds
- Can a consistent and defensible method for evaluating environmental significance of a small-volume release be developed?
- What are the data requirements?



Conceptual Model for Small-Volume Release

$C_o(t)^* = J_z(t)/q_x(t)$ or $C_{well}^* = J_z(t)/J_{well}$



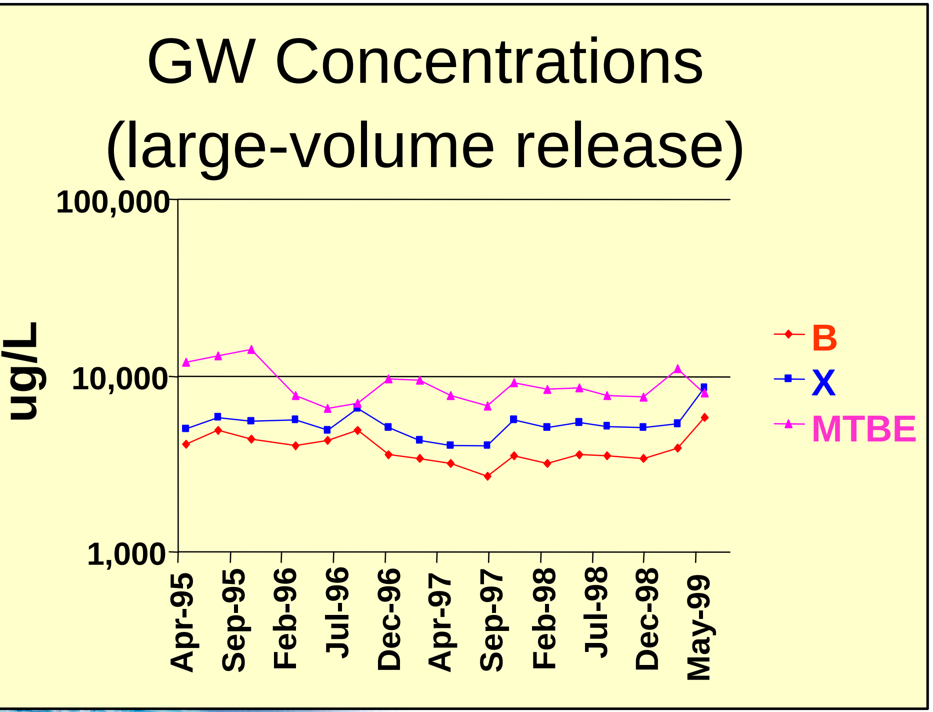


***assumes no mixing/dilution/dispersion in ground water**

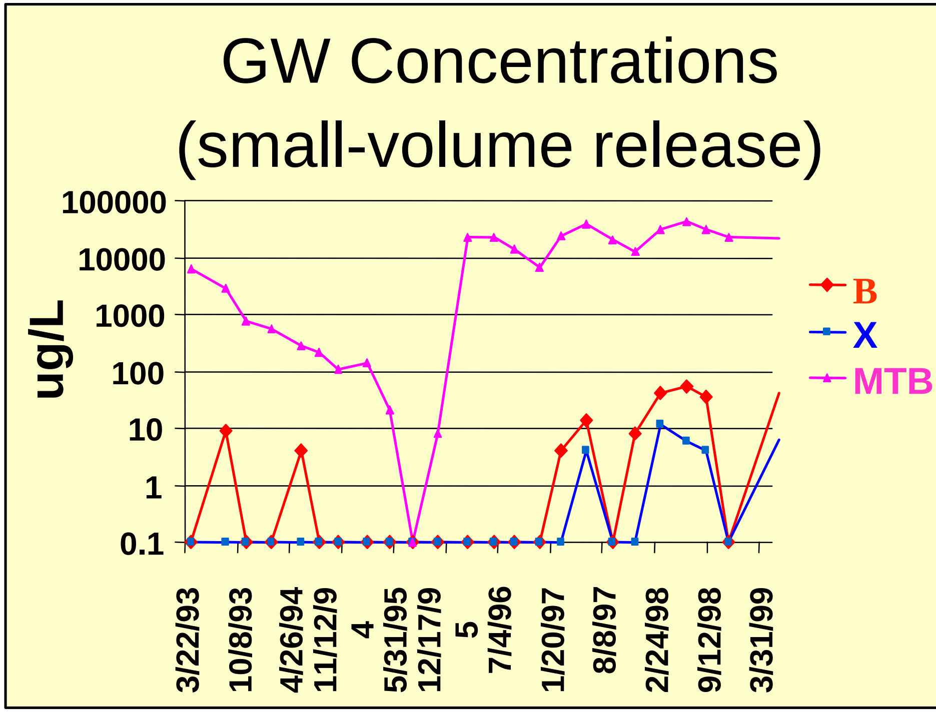
Field Data: Ground Water in Source Area

<u>MTBE : benzene</u>
Theory ~ 200 : 1

Observed ~ 15 : 1



Observed >> 100 : 1

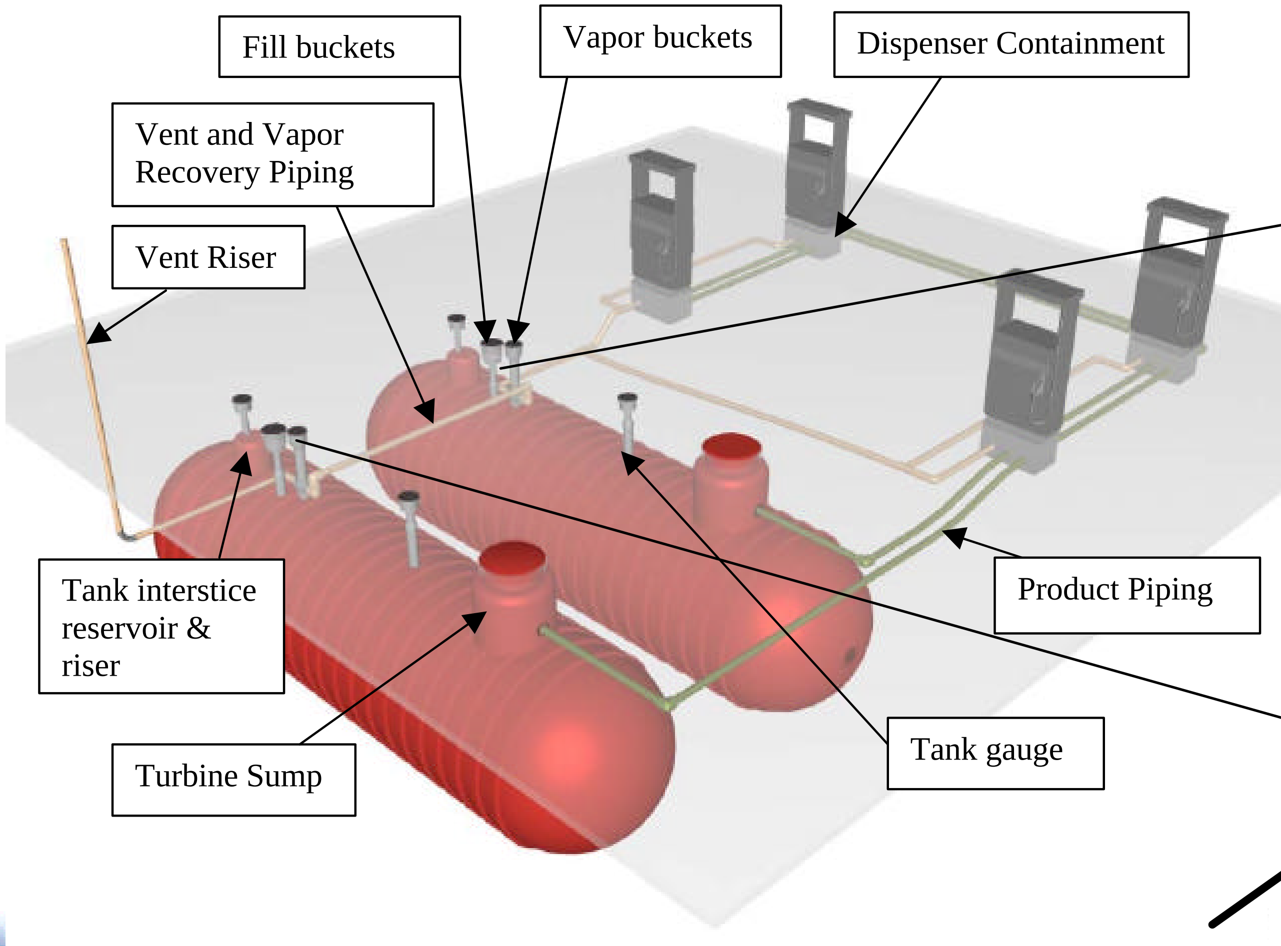


Frequency and Occurrence

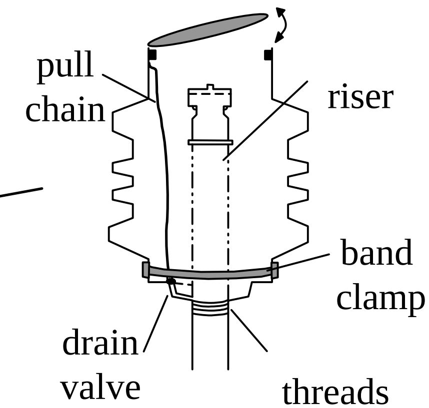
- UC-Davis/Tracer Research Corp./Ca SWRCB (2002)
  - 182 randomly selected UST systems - 55 locations
  - tracer releases: 61% vapor related; < 1 % liquid related
    - tank tops equipment (risers buckets) suspected
    - release rates (estimated < 0.04 gal/d - liquid equiv.)
  - uncertainties with investigation
    - no field validation* (release type, additional sources?)
    - tanks connected in series (which tank?, how many?)
    - difficult to correlate with release rate
    - transfer value?

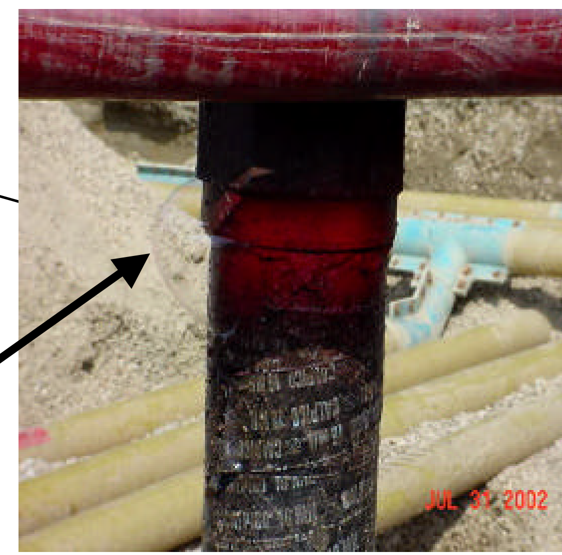
http://www.swrcb.ca.gov/cwphome/ust/docs/fbr/index.html

UST System



Spill bucket design





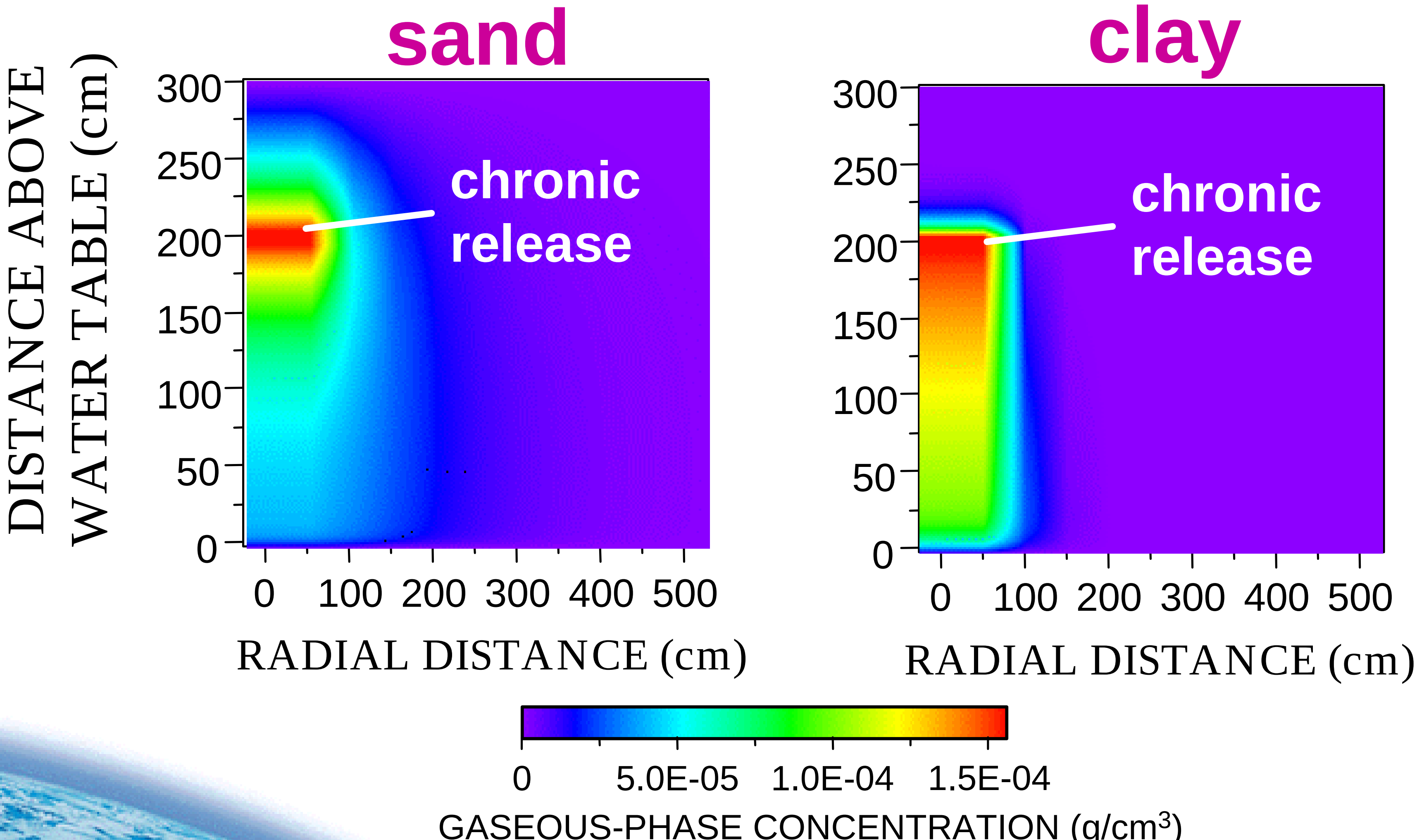
Previous Studies

- API Study (Lahvis and Rehmann, 2000 -- API Tech. Research Bulletin No.10
- API Study (Lahvis, 2003 -- API Tech. Research Bulletin, *in press*)
- Dakhel et al., 2003 (ES&T)

RESULTS indicate primarily an issue for MTBE, not EtOH

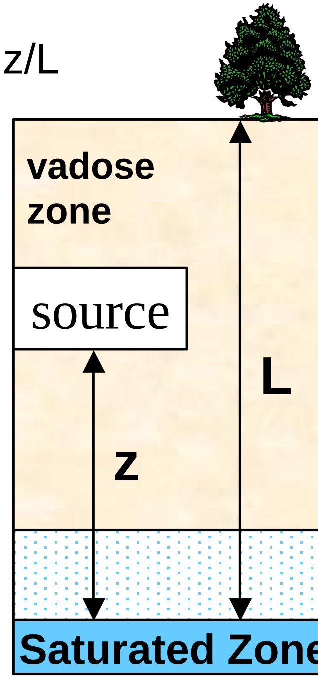
Steady-State MTBE Distribution

(infiltration rate = 20 cm/yr)



Conclusions

- MTBE
  - ppm-level concentrations in ground water are possible
  - impacts are most sensitive to infiltration -- less sensitive to soil type, depth to ground water
  - mass losses to atmosphere can be significant
    - o e.g., 6 % of initial source mass reaches gw - sand, no infiltration, z/L = 0.67
    - o *f* (infiltration rate, soil type, relative distance of source above water table - z/L

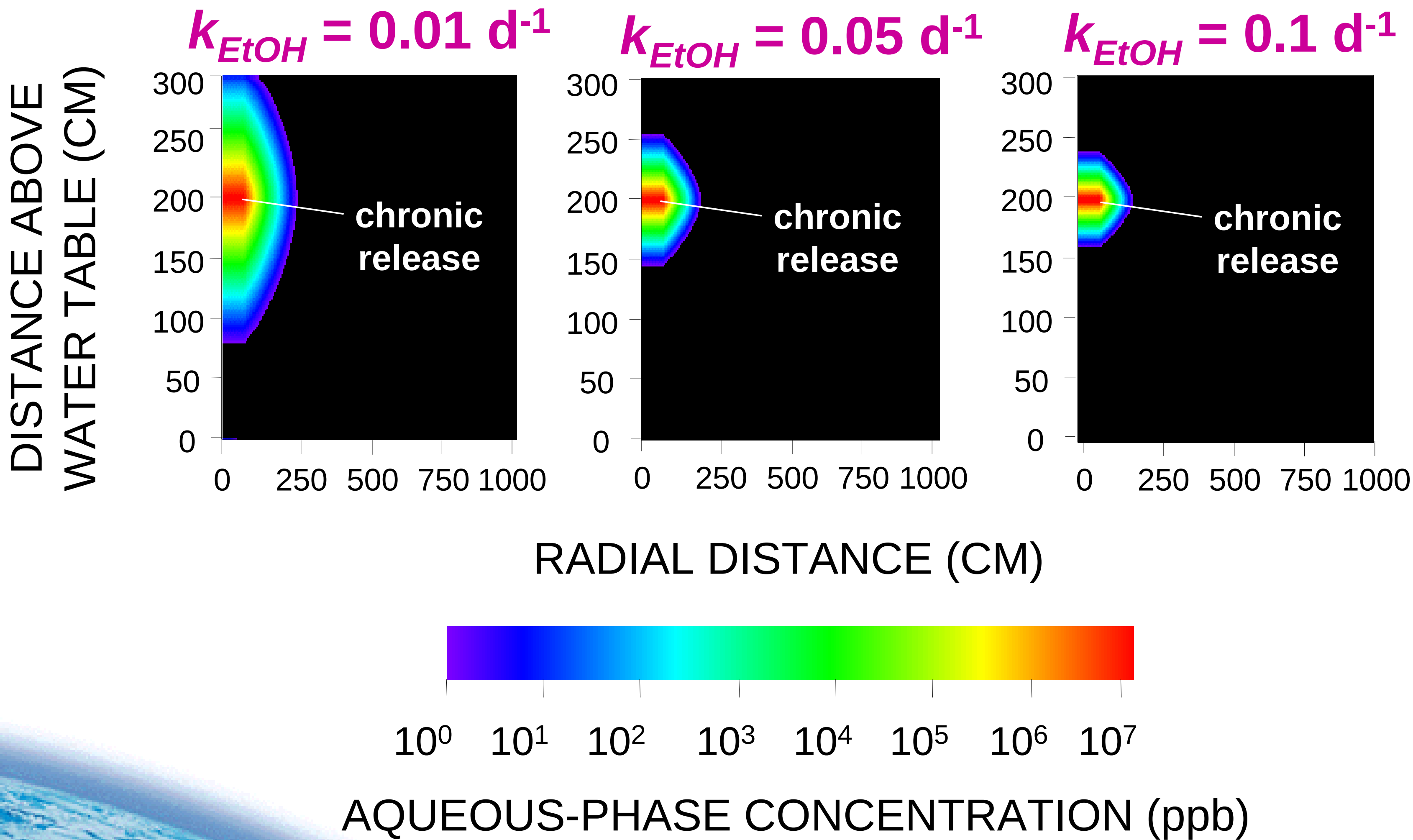


- Benzene
  - impact *f* (O_2 availability) - release history, competing sources?
  - capillary zone is barrier

- Breakthrough times (days to years)
  - *f* (soil type, depth to ground water)

Steady-State EtOH Distribution -- f (bio. rate - k_{EtOH}

[sand, no infiltration]



Conclusions

- EtOH
  - transport in vadose zone (under anticipated conditions)
    - biodegradation critical
    - no effect on benzene transport

- Travel times 2x to >20x greater for EtOH than for benzene

- Larger volume release, neat EtOH?

Dakhel et al., (2003)

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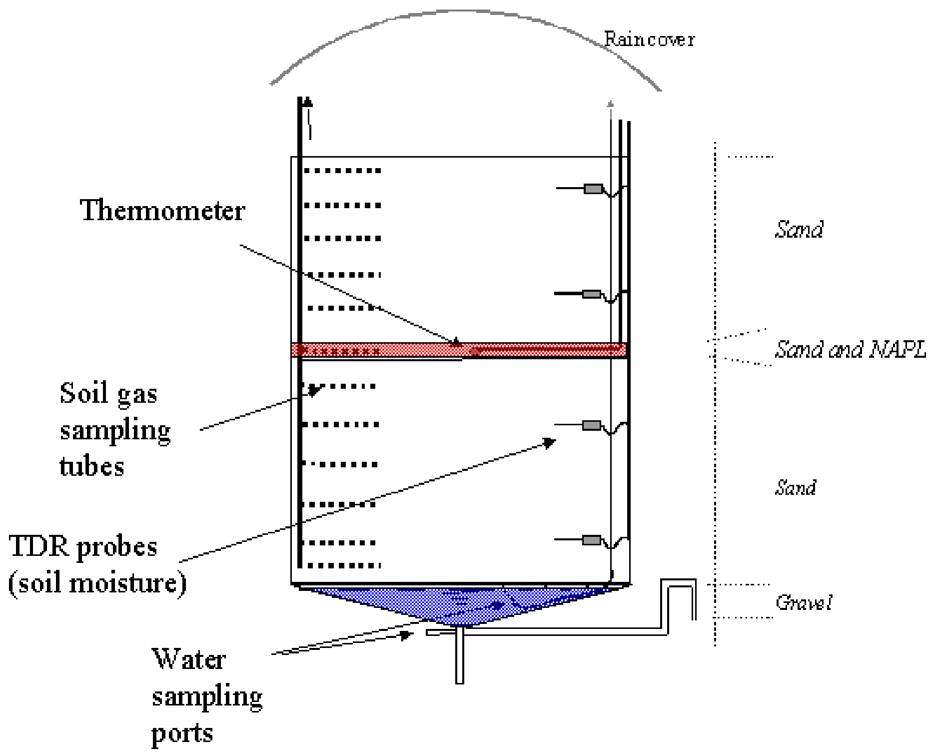
- MTBE
  - validation of API model results
- EtOH
  - migration to ground water not observed unless subject to significant infiltration (182 cm/yr)
  - biodegradation sole removal mechanism



Set-up of the lysimeter experiment (Pasteris et al., 2002)

Evaluating the Potential for Ground-Water Contamination

(*Lahvis and Baehr*, 1999 -- USGS WRIR 99-4018C)

- Focus on:
  - BTEX
    - MTBE phased out in CA by Shell
    - EtOH not expected to be an issue unless source is very near (< 0.5 m) water table
  - evaluation of potential impacts on ground water achieved through site characterization and type-curve analysis

Evaluating the Potential for Ground-Water Contamination

Governing Transport Equation

$$D\frac{\partial^2 C}{\partial z^2} - q\frac{\partial C}{\partial z} - l\,C = 0$$

iffusion

advection
(gw infiltration)

biodegradation

D = effective diffusion coefficient
q = ground-water infiltration rate
l = biodegradation rate
C = aqueous-phase concentration
z = distance above water table

Transformed Equation
(dimensionless analysis)

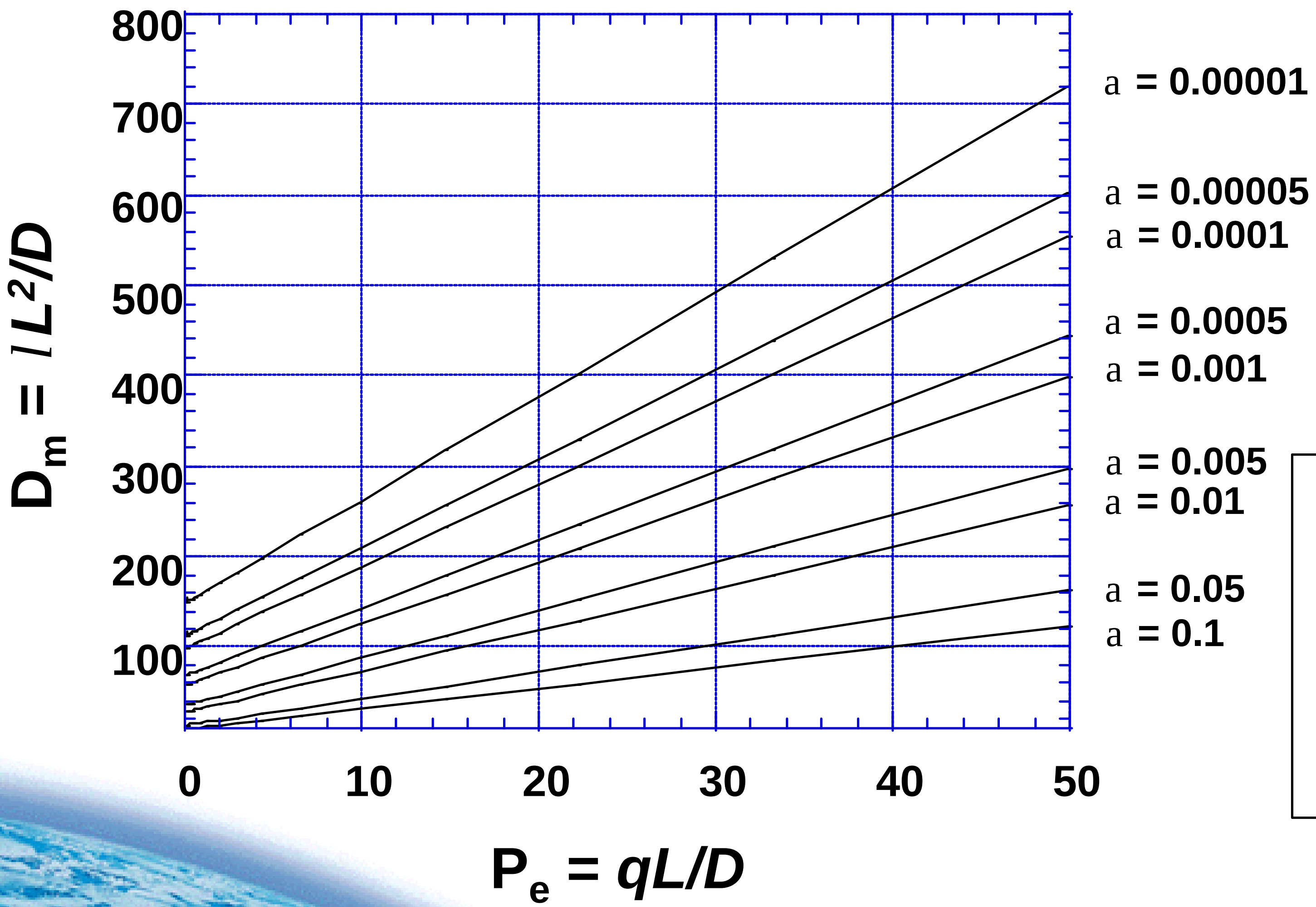
$$\frac{\partial^2 C}{\partial x^2} - P_e\frac{\partial C}{\partial x} - D_m C = 0$$

where,

$$P_e = \frac{qL}{D},\quad D_m = \frac{l\,L^2}{D},\quad x = \frac{z}{L}$$

P_e = Peclet Number (scales advection and diffusion)
D_m = Damkohler Number (scales biodegradation and diffusi

Type Curve Analysis



attenuation coefficient

a = C_{wat}/C_o

Examples

q (cm/yr)	18	
L (ft)	4	
	Benzene	*EtOH*
D (cm²/s)	0.001	1.5E-06
λ (1/d)	0.01	0.1
D_m	1.8	11,500
P_e	0.1	46

Evaluating the Potential for Ground-Water Contamination For Small-Volume Releases

- Step 1) Site Characterization to confirm “small-volume release” CSM
  - identify/delineate source(s)
  - soil-gas data (**measure C_i^{benz} and C^{O2}**)
  - soil data (soil type, presence of NAPL, stratigraphy)
  - ground water data
  - **depth to ground water below source (*L*) or from any soil-gas probe location (L_i)**
- Step 2) Predict $C_{wat}(a_i)$ based on calculated P_e and D_m, C_i^{benz}, and L_i
- Step 3) Compare estimates of a_i obtained from C_i^{benz} and L_i
- Step 3) Monitor potential migration to ground water

$$P_e = \frac{qL}{D}$$

$$D_m = \frac{\lambda L^2}{D}$$

Default values: *D(benzene)* = 0.001 cm²/s (EPA, 1996)
q = 18 cm/yr (EPA,1996)
λ^* = 0.01 d^{-1} (aerobic) Howard (1991)
λ = 0.001 d^{-1} (anaerobic) Howard (1991)

*** requires confirmation of O_2 availability**

Test the Method (i.e. $l = 0.01$ d^{-1}) w/ Site Data

- compare observed vs. predicted attenuation at 6 suspected small-volume release sites to see if $\lambda = 0.01$ d^{-1} is conservative
- problem…no sites with adequate soil-gas concentration data and small-volume release CSM
- assumed soil-gas concentration at source is 10% of benzene concentration in equilibrium with gasoline containing 1% v/v benzene
- calculated observed attenuation based on max. benzene conc. (measured)

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
C_o *(ppb)	1,700	1,700	1,700	1,700	1,700	1,700
C_{wat} **(ppb)	0.77	ND	16	100	1.7	0.59
a (observed)	0.0005	--	0.009	0.06	0.001	0.0003

= hypothetical

Predict Attenuation w/ Site Data

Compute values of D_m and P_e

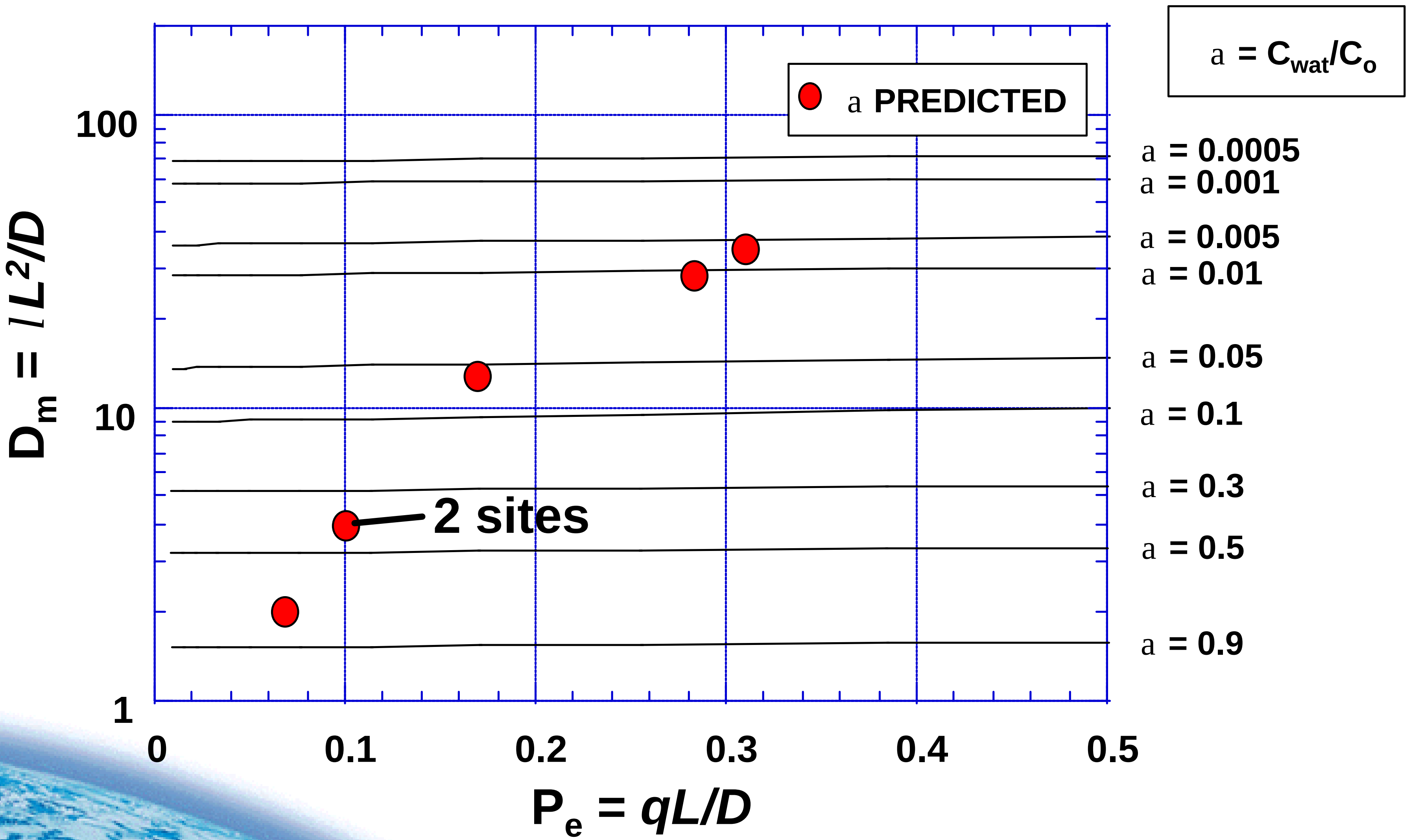
$$P_e = \frac{qL}{D}$$

$$D_m = \frac{l L^2}{D}$$

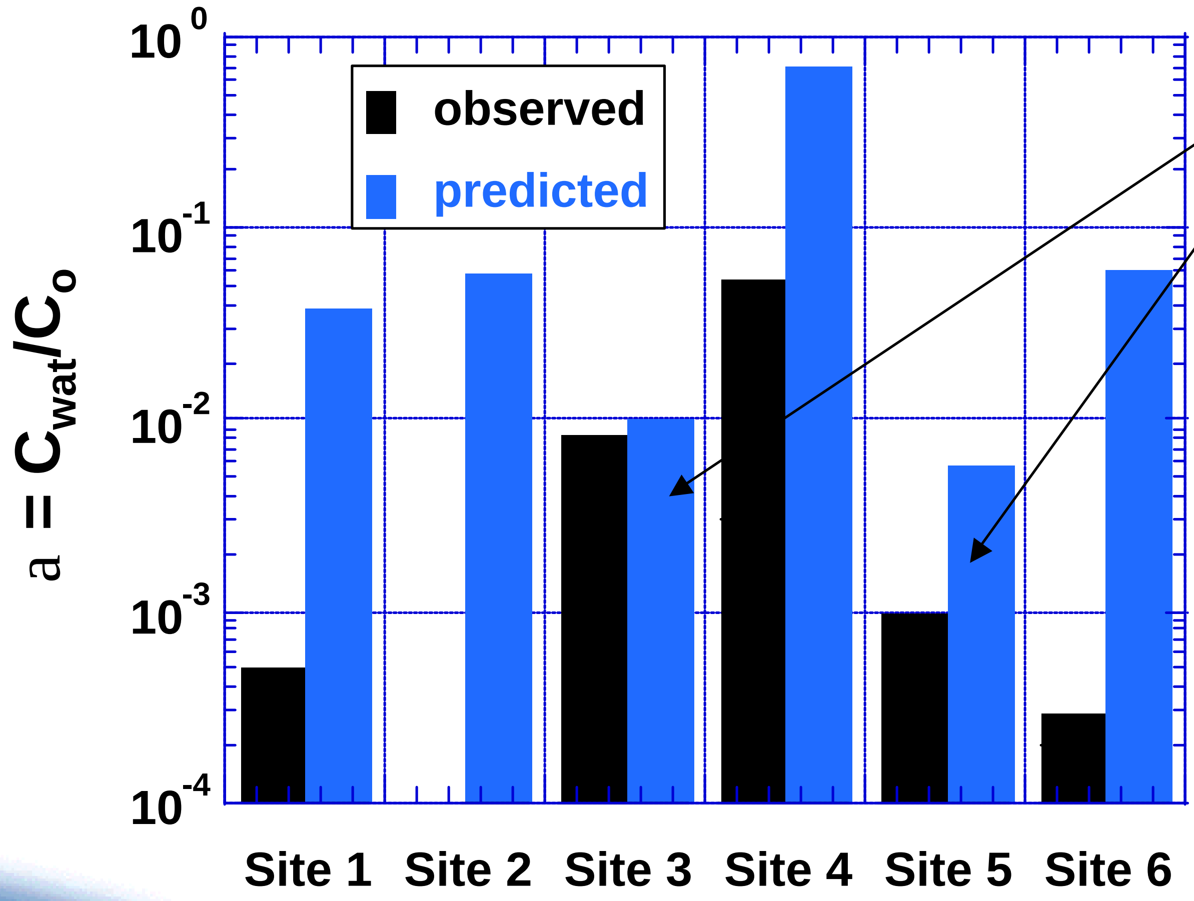
l (d^{-1})	**0.01**
q (cm/yr)	**18**
D (cm^2/s)	**0.001**

	Site 1	**Site 2**	**Site 3**	**Site 4**	**Site 5**	**Site 6**
L(ft)	**6**	**10**	**16**	**4**	**18**	**10**
P_e	**0.1**	**0.17**	**0.28**	**0.07**	**0.31**	**0.17**
D_m	**4**	**11**	**28**	**2**	**34**	**11**

Predict Attenuation



Comparison of α (observed) with α (predicted)



Small-Volume Release?

Site 3 : benzene/MTBE = 7

Site 5 : ethylbenzene/MTBE = 1.5

l = 0.01 d^{-1} appears to be conservative (C^{benz} and C^{O2} validation required)

Conclusions

- Recent evidence suggests that vapor releases are more common than liquid releases, however, their risk to ground water needs to be quantified on a site-by-site basis.

- The environmental significance of vapor (or small-volume liquid) releases can be determined based on transport in the vadose zone.

- Approach requires confirmation of conceptual model (site characterization) and type-curve analysis.

- Key parameters are C, L, and λ
  - benzene impacts not anticipated for L > 20 ft. if aerobic biodegradation is occurring for small-volume releases
  - selection of λ will depend on O_2 availability

- Method can be applied for other reactive constituents